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### Research paper

# Facile synthesis of heterostructured YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalysts with enhanced visible-light photocatalytic performance



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#### ABSTRACT

A series of YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composite photocatalysts with various concentrations of YVO<sub>4</sub> (YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag) were synthesized for the first time by hydrothermal and the photodeposition method. The photocatalytic activity of the as-prepared YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composites was evaluated by the degradation of methyl orange (MO) under visible light irradiation. It shows that the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> can be largely enhanced by loading Ag nanoparticles (NPs) and YVO<sub>4</sub> NPs together. The optimized loading content of YVO<sub>4</sub> is 35 wt%, and the highest rate constant shown in 35 wt% YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag is 0.03404 min<sup>-1</sup>, about 3 times and 2.1 times higher than that in g-C<sub>3</sub>N<sub>4</sub> (0.01131 min<sup>-1</sup>) and g-C<sub>3</sub>N<sub>4</sub>/Ag (0.01613 min<sup>-1</sup>), respectively. The surface plasmon resonance (SPR) of Ag NPs and efficiently suppressed recombination of charge carriers due to the introduction of YVO<sub>4</sub> NPs make the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag nanocomposite photocatalysts exhibit excellent visible photocatalytic performance and excellent photocatalytic stability. In addition, the trapping experiments using different scavengers showed that the reactive O<sub>2</sub>· and ·OH play the major role in the photodegradation of MO.

#### 1. Introduction

In the modern society, energy crisis and environmental pollution have become the vital problems facing human beings [1–4]. Exploring an efficient way to solve these two problems has been one of the hottest research topics [5]. Photocatalysis is attracting more and more attention in photodegradation of organic pollutants for environmental remediation due to the redox capacity of photocatalysts driven by solar energy [1,6–9]. Up to date, considerable efforts have been made to develop green, renewable, efficient and broadband photocatalysts.

As two-dimensional (2D) nanosheets of tri-s-triazine, polymeric graphitic carbon nitride (g- $C_3N_4$ ) has been considered as one "sustainable" material for photocatalysis, because of its facile preparation process and the abundant and low-cost raw material [10,11]. Furthermore, being different from other polymer materials, the g- $C_3N_4$  possesses thermal stability, as well as acidic and alkaline resistance. But above all, the g- $C_3N_4$  can absorb visible light up to 450 nm due to its relatively narrow band gap (2.7 eV) [12], and has been recognized as one of the potential candidates of visible-light photocatalysts. However, there are still some shortcomings that restrict the practical applications

of g- $C_3N_4$ , such as the small surface area, high recombination rate of photogenerated electron-hole pairs, and the poor absorption of the visible light with the wavelength longer than 450 nm [13–16]. To address these issues, numerous strategies have been proposed to facilitate the charge carriers separation and transportation and extend the absorption range towards longer wavelengths, for example, the coupling with narrower-band gap semiconductors, doping with metallic and nonmetallic elements, and introducing carbonaceous material [17–22], etc.

Recently, the orthovanadates, such as  $BiVO_4$ ,  $InVO_4$  and  $YVO_4$ , etc., have been studied as photocatalysts with good performance in the water splitting and/or photodegradation [23–25]. It is known that  $YVO_4$  has a wide band gap (3.38 eV), which can only be excited by UV light, but the excited charge carriers exhibit stronger redox capability [25,26]. Therefore, the coupling of  $g-C_3N_4$  with  $YVO_4$  is a possible approach to make the composite possess improved visible-light photocatalytic activity, which has been seldom been reported yet. However, the limited range in the utilization of visible light and the fast recombination of charge carriers remain unsolved through the combination of  $g-C_3N_4$  and  $YVO_4$ .

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The noble metallic nanoparticles (NPs), such as Au and Ag, have attracted considerable attention to enhancing the visible light activity of photocatalysts due to their surface plasmon resonance (SPR) effect [27–32]. In the case of Ag/g-C<sub>3</sub>N<sub>4</sub>, Ag NP can broaden the light absorption of g-C<sub>3</sub>N<sub>4</sub> over a wide range via the SPR effect; furthermore, Ag NP can act as the electron reservoir, promoting the transfer of charge carriers and suppress their recombination [33,34]. For example, Chen et al. reported that the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> could be enhanced by introducing the Ag NPs in the degradation of Rhodamine B [35]. Zhu et al. prepared Ag@C<sub>3</sub>N<sub>4</sub> core-shell plasmonic composite and obtained enhanced photocatalytic activity originated from a combined result of the SPR effect of Ag and hybrid effect from C<sub>3</sub>N<sub>4</sub> [33].

In this paper, the ternary composite of heterostructured YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst was designed and synthesized for the first time. A series of composite photocatalysts with 2 wt% Ag and various amount of YVO<sub>4</sub> were prepared by the hydrothermal and photodeposition method. The composite photocatalysts exhibited enhanced photocatalytic performance in the degradation of methyl orange (MO) under visible-light irradiation (> 420 nm), remarkably suggesting that the combined effects of the SPR of Ag NPs and the coupling with YVO<sub>4</sub> NPs which efficiently suppress the charge carriers recombination. Moreover, the possible mechanism involved in the photocatalytic reaction was proposed in detail.

#### 2. Experimental details

#### 2.1. Materials

The initial chemicals, including  $Y_2O_3$  ( $\geq 99.99\%$ ) which was purchased from GZSUNKO new material company, and other chemicals were purchased from Beijing Chemical Company, China. All chemicals were reagent grade and were used directly without further purification. Rare earth chloride stock solutions (0.2 M) were prepared by dissolving the corresponding metal oxide in HCl acid under stirring.

# 2.2. Preparation of YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag nanocomposites

The synthesis procedures of  $YVO_4/g$ - $C_3N_4/Ag$  nanocomposites are shown in Fig. 1. The g- $C_3N_4$  was obtained by calcining a certain amount of urea. Typically, 5 g of urea was placed in a covered alumina crucible and thermally treated at 550 °C for 4 h with a heating rate of 1 °C min  $^{-1}$  under air atmosphere. The yellow-colored product was collected and ground into powder for further use.

The YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites were prepared by a hydrothermal method. Typically, 0.25 g of g-C<sub>3</sub>N<sub>4</sub> was dispersed into 20 mL of deionized water under ultrasonication for 0.5 h, and then YCl<sub>3</sub> solution and NH<sub>4</sub>VO<sub>3</sub> were added slowly to the dispersion with the same molar of Y<sup>3+</sup> and V<sup>5+</sup>. After ultrasonication for another 0.5 h, the mixture was transferred into a 100 mL a Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 180 °C for 6 h. After naturally cooling down to room temperature, the solid product was collected and washed thoroughly by centrifugation with deionized water, and then dried at 80 °C for 12 h. For comparison, pure YVO<sub>4</sub> was prepared using the same method, except for not adding g-C<sub>3</sub>N<sub>4</sub> sheets to the YVO<sub>4</sub> solution.

The YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalysts were prepared by a simple photodeposition method. As photodeposition is an appropriate approach to prevent NPs from aggregation, it can be used to prepare supported Ag NPs with highly dispersed active sites [36]. Specifically, the as-prepared YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> powder (0.10 g) was dispersed into the AgNO<sub>3</sub> aqueous solution. The resulting suspension was irradiated under a 300W Xe lamp for 2 h. Then the powder separated by centrifugation was washed with deionized water. Finally, the product was dried at 80 °C for 12 h.

#### 2.3. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a D8 Focus diffractometer (Bruker) with use of Cu Ka radiation  $(\lambda = 0.154 \text{ nm})$ . Fourier transform infrared (FT-IR) spectra were measured with a Nicolet Magna 560 infrared spectrophotometer with the KBr pellet technique. ESCALAB 250 spectrometer (Thermo Electron Corporation, UK) equipped with an Al Ka source and a charge neutralizer was used to measure X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). All the spectra were calibrated to the C1s peak at 284.6 eV of the adventitious carbon. Transmission electron microscopy (TEM) was performed by using an FEI Tecnai G<sup>2</sup> S-Twin instrument with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multipole CCD camera. The UV-vis diffuse reflectance spectra (DRS) of catalysts were recorded on a UV-vis spectrometer (U-4100; HITACHI, Tokyo, Japan) equipped with an integrating sphere. The photoluminescence (PL) spectra were measured by using a fluorescence spectrophotometer (F4600, Hitachi, Japan) with the excitation wavelength of 300 nm.

#### 2.4. Photocatalytic experiment and the detection of active species

The photocatalytic performances of the as-prepared YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/ Ag photocatalysts were investigated by photodegrading MO dye in aqueous solution. 20 mg of the as-prepared photocatalysts were added to 20 mL of the MO aqueous solution (20 mg L<sup>-1</sup>) in a quartz flask (50 mL in capability), and was magnetically stirred for 30 min in the dark to reach the desorption - absorption equilibrium. A 300 W xenon lamp filtered by a UV cut-off filter ( $\lambda > 420 \, \text{nm}$ ) was used as the visible light source. At certain time intervals, 0.6 mL of the reaction solution was taken out and centrifuged to remove the catalyst, then analyzed on UV-vis spectrometer to detect the residual concentration of MO in the solution. In addition, in order to detect the generated active species in the photocatalysis, 1,4-benzoquinone (BQ) (1 mM), disodium ethylenediaminetetraacetate (Na<sub>2</sub>EDTA) (1 mM), and tert-butyl alcohol (t-BuOH) (1 mM) were used as superoxide radical (·O<sub>2</sub><sup>-</sup>), hole, and hydroxyl radical (OH) scavengers, respectively, with all other conditions being the same.

#### 3. Results and discussion

## 3.1. Characterization of prepared samples

The crystallinity and phase purity of the as-prepared samples were characterized by XRD (Fig. 2). For the pure YVO<sub>4</sub> (Fig. 2A), it can be

Calcining urea Dispersion Hydrothermal YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> AgNO<sub>3</sub> VVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> AgNO<sub>3</sub> VVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> Ag

Fig. 1. Schematic illustration for the synthesis of the  $YVO_4/g$ - $C_3N_4/Ag$  nanocomposite.

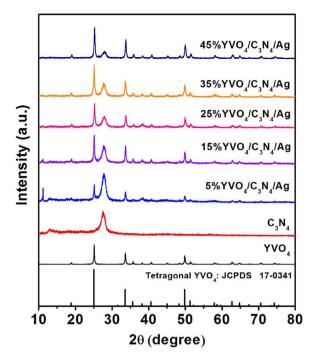


Fig. 2. XRD patterns of YVO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>, and YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag samples with different contents of YVO<sub>4</sub> from 15 wt% to 45 wt%.

seen that all the diffraction peaks of the sample can be readily indexed to a pure tetragonal phase of YVO<sub>4</sub> (space group: I4<sub>1</sub>/amd) according to the JCPDS file No. 17-0341 (a = b = 7.1192 Å and c = 6.2898 Å). The well-resolved diffraction peaks, no peaks shifts, and other impurity phases appearance indicates the high crystallinity and purity of the asprepared sample [37]. As for the pure g-C<sub>3</sub>N<sub>4</sub> sample (Fig. 2B), it shows diffraction peaks at 13.1° and 27.4°, which can be indexed as the (100) crystal plane of tri-s-triazine units and the (002) diffraction for interlayer stacking of aromatic systems of graphitic materials, respectively [38,39]. For the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composites (Fig. 2C-G), the XRD patterns show YVO4 and g-C3N4 phases. With an increasing amount of YVO<sub>4</sub> from 5.0% to 45.0%, the diffraction peaks of YVO<sub>4</sub> are intensified gradually, whereas the peaks of g-C<sub>3</sub>N<sub>4</sub> are weakened. However, due to the quiet low loading amount and the overlapping of diffraction peaks in all these samples, the diffractions of Ag NPs could not be observed. The peaks at 27.4° in YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag samples suggest that the structure of g-C<sub>3</sub>N<sub>4</sub> is not changed by the hydrothermal treatment.

For further confirming the formation of the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composites, the FT-IR spectra of the as-prepared products were also measured (Fig. 3). As shown in Fig. 3A, the YVO<sub>4</sub> sample has a strong characteristic peak at 820 cm<sup>-1</sup>, which can be attributed to the V-O stretching vibration mode (from the VO<sub>4</sub><sup>3-</sup> group) [40]. For the bare g-C<sub>3</sub>N<sub>4</sub> sample (Fig. 3B), the peak at 812 cm<sup>-1</sup> is attributed to the characteristic breathing modes of triazine units [41]. The peaks at 1641, 1580, 1465, 1404, 1323, and 1242 cm<sup>-1</sup> are associated with the stretching vibrations of CN heterocycles [42]. The broad peak at 3000-3650 cm<sup>-1</sup> was assigned to the stretching vibration modes of terminal N-H and O-H [43]. All the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composites exhibit similar peaks as the g-C<sub>3</sub>N<sub>4</sub> sample. With the increase of YVO<sub>4</sub> amount, this band was affected and shifted towards the higher wavenumber due to the presence of the absorption band of YVO4 at  $820~\text{cm}^{-1}$ . This is another evidence for the introduction of  $YVO_4$  into g- $C_3N_4$ .

The surface chemical composition and status of elements in the  $YVO_4/g$ - $C_3N_4/Ag$  sample were further analyzed by XPS (Fig. 4). Fig. 4a shows the XPS survey spectrum of the  $YVO_4/g$ - $C_3N_4/Ag$  composite, which suggests that sample primarily consists of Y, V, O, C, N and Ag elements without other impurities. As displayed in Fig. 4B, the V2p

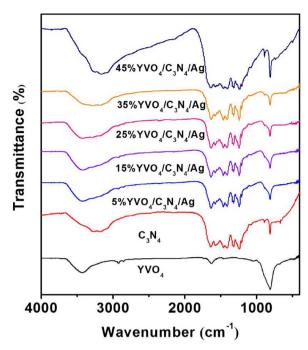


Fig. 3. FT-IR spectra of  $YVO_4$ ,  $g-C_3N_4$ , and  $YVO_4/g-C_3N_4/Ag$  samples with different contents of  $YVO_4$  from 15 wt% to 45 wt%.

states split into two lines  $V2p_{1/2}$  (524.6 eV) and  $V2p_{3/2}$  (517.1 eV) with an energy splitting of 7.5 eV because of the spin-orbit interactions [44,45]. In addition, the difference of binding energy between the  $V2p_{3/2}$  and the O 1 s (530.0 eV) is about 12.9 eV, confirming the presence of  $V^{5+}$  oxidation state [44]. Fig. 4C shows that the Y3d state was fitted into two peaks,  $Y3d_{3/2}$  (159.3 eV), and  $Y3d_{5/2}$  (157.2 eV). Meanwhile, the ultraviolet photoelectron spectroscopy (UPS) was carried out to determine the VB position of  $YVO_4$  (Fig. 4D). The VB maximum potential was calculated to be 2.61 eV, which is consistent with the previously reported work [44].

The morphology and microstructure of the as-prepared samples were further observed by TEM technique (Fig. 5). For YVO<sub>4</sub> sample (Fig. 5A), irregularly shaped nanoparticles can be observed. Fig. 5B shows the typical TEM image of g-C<sub>3</sub>N<sub>4</sub>, which exhibited 2D sheet-like nanostructures with transparent thin layers resembling the graphene nanosheets. Upon incorporating Ag NPs, the TEM image (Fig. 5C) shows that the Ag NPs are uniformly dispersed on the surface of g-C<sub>3</sub>N<sub>4</sub> nanosheets. The YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composite with the YVO<sub>4</sub> NPs and Ag NPs supported on the g-C<sub>3</sub>N<sub>4</sub> nanosheets is displayed in Fig. 5D. It can be seen that the YVO4 NPs and Ag NPs were randomly distributed on the surface of g-C<sub>3</sub>N<sub>4</sub> sheets. The TEM characterization also confirms the successful synthesis of YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composites, which are consistent with the XRD and FT-IR analysis. The high-resolution TEM (HRTEM) image of YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag displays the interface and spatial arrangement of these three components (Fig. 5E). The lattice fringes with inter-plane distances of 0.32 nm and 0.24 nm correspond to the (200) planes in the tetragonal YVO<sub>4</sub> structure [46], and the (111) plane of the face-centered cubic Ag NPs [47], respectively. Furthermore, the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composite was ultra-sonicated for 1 h for TEM analysis, indicating that the interaction among these three components is very strong, which is particularly favorable for the photocatalysis.

The optical absorption properties of all the samples were measured by the UV–vis spectrometer (Fig. 6). Fig. 6A shows the UV–vis absorption spectra of pure g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/Ag and the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag with different YVO<sub>4</sub> contents. A shown in the absorption spectra, pure g-C<sub>3</sub>N<sub>4</sub> and all the samples contain g-C<sub>3</sub>N<sub>4</sub> show visible light absorption with absorption edge around 465 nm. For the samples with Ag, the extra broad absorption band centers at  $\sim 500$  nm was also observed,

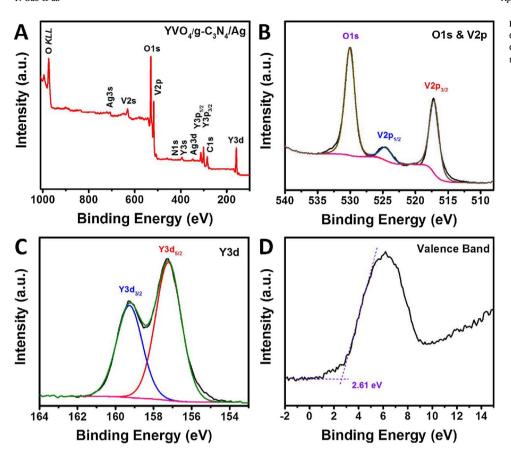


Fig. 4. (A) XPS survey spectra, (B) high-resolution O1 s and V2p, (C) high-resolution Y3d of YVO $_4$ /g-C $_3$ N $_4$ /Ag, and (D) UPS spectrum of YVO $_4$  to determine its VB position.

which is attributed to the SPR of Ag NPs [48–50]. As shown in Fig. 6B, the YVO<sub>4</sub> can only absorb the UV light with the absorption edge around 363 nm. According to the Kubelka-Munk function [39], the band gap energy of YVO<sub>4</sub> can be estimated to be 3.42 eV. Considering that the VB maximum of YVO<sub>4</sub> is 2.61 eV and its band gap energy is 3.42 eV, the CB minimum is calculated to be -0.81 eV.

# 3.2. Photocatalytic performance

The photocatalytic activity of YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composite was

assessed by the photodegradation of MO at room temperature under visible light ( $\lambda > 420$  nm) irradiation. Meanwhile, we also tested the blank experiment under the same condition to investigate the photostability and chemical stability of MO. After 120 min, no MO was degraded without the help of the photocatalyst, indicating that MO is a suitable model dye with high stability under visible light irradiation. Fig. 6A shows the decrease of MO concentration as a function of time over different photocatalysts. The concentration of MO is unchanged after 2 h in the presence of YVO<sub>4</sub> under visible light irradiation. As expected, the g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/Ag show visible light activity in the

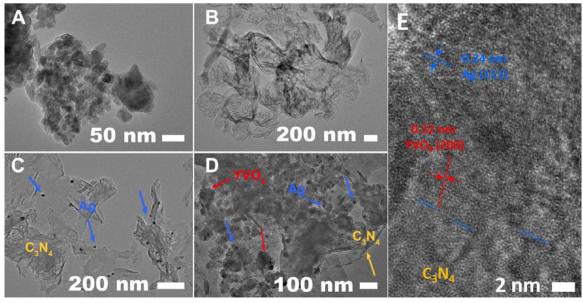


Fig. 5. TEM images of (A) YVO<sub>4</sub>, (B) g-C<sub>3</sub>N<sub>4</sub>, (C) g-C<sub>3</sub>N<sub>4</sub>/Ag, (D) YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag, and (E) HRTEM image of YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag sample.

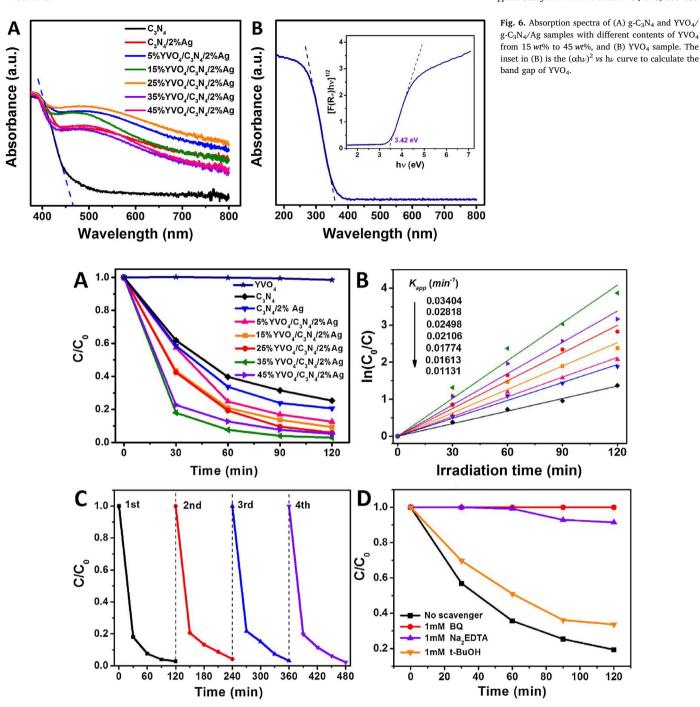


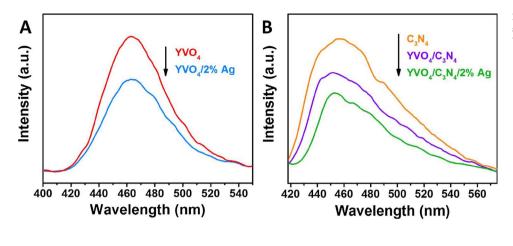
Fig. 7. (A) The photodegradation activities of MO as a function of time over different photocatalysts under visible light irradiation, (B) plot of  $\ln(c_0/c)$  vs time and the apparent reaction rate constant, (C) cycling runs of 35 wt VVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst in the photodegradation of MO, and (D) photodegradation of MO in the presence of three types of scavengers and 35 wt VVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst under visible light irradiation.

photocatalytic degradation of MO. After the introduction of YVO<sub>4</sub>, the photocatalytic degradation rate was increased compared with the g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/Ag samples, because of the restrained recombination of charge carriers. The optimal content of YVO<sub>4</sub> in YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag was found to be 35 wt% by comparing their photocatalytic efficiency in the degradation of MO solution.

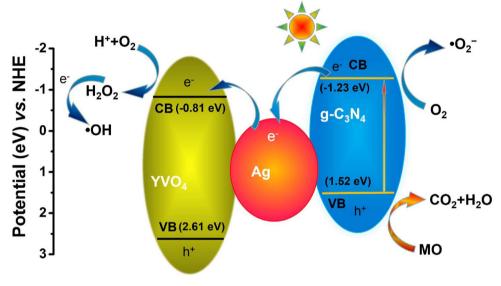
With increasing the concentration of  $YVO_4$  over 35%, the photocatalytic degradation rate starts to decrease, which is because that the covering of excessive  $YVO_4$  on the surface of  $g\text{-}C_3N_4$  leads to the poor optical penetration.

For the kinetic study of different photocatalysts, the photocatalysis data were fitted with the pseudo-first-order model (Fig. 5B). The

equation is  $\ln(C_0/C) = kt$ , where  $C_0$  and C are the concentrations of MO at irradiation time of 0 and t, respectively, and k is the apparent reaction rate constant. Fig. 5B shows that the photocatalytic degradation of MO, in the presence of as-prepared photocatalysts under visible light irradiation, which matches well with the pseudo-first-order model. As displayed in Fig. 5C, the highest rate constant  $(0.03404 \, \text{min}^{-1})$  is achieved by the 35%  $YVO_4/g-C_3N_4/Ag$  sample, which is about 3 times higher than the pure  $g-C_3N_4$  sample  $(0.01131 \, \text{min}^{-1})$ , and about 2.1 times higher than the  $g-C_3N_4/Ag$  sample  $(0.01613 \, \text{min}^{-1})$ . To be served as a good photocatalyst, except for the enhanced visible light activity, the reusability and stability are also extremely important. The photocatalytic degradation of MO under visible light was carried out for 4



**Fig. 8.** PL spectra of the (A) YVO<sub>4</sub> and YVO<sub>4</sub>/Ag samples, and (B) g-C<sub>3</sub>N<sub>4</sub>, YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> and 35 *wt*% YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag samples.



**Fig. 9.** Photocatalytic mechanism scheme over YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst under visible-light irradiation.

cycles in the presence of 35% YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst (Fig. 5C). After 4 consecutive cycles, the 35% YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag still shows very high photocatalytic degradation rate of MO. This result indicates that the as-prepared YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst possesses excellent reusability and photostability.

In order to detect the main active species in the photocatalytic process, such as photogenerated holes, superoxide radicals ( $\cdot O_2^-$ ) and hydroxyl radicals ( $\cdot OH$ ), the trapping experiments in the presence of various scavengers were operated. As shown in Fig. 7, under the visible light irradiation of the as-prepared YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst, the photodegradation rate of MO was slightly suppressed by the addition of  $\cdot OH$  radical scavenger (t-BuOH, 1 mM), which reveals that  $\cdot OH$  radicals are not the main active species for the photodegradation of MO in current photocatalytic systems. However, in the presence of the  $\cdot O_2^-$  radical scavenger (BQ, 1 mM) and the hole scavenger (Na<sub>2</sub>EDTA, 1 mM), the photodegradation rate of MO was decelerated significantly, with the photocatalytic degradation rate being reduced by 67.2% and 37.1%, respectively. It means that the  $\cdot O_2^-$  and  $\cdot OH$  radicals play the major roles in the photodegradation of MO over the as-prepared YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag photocatalyst under visible light irradiation.

The PL spectra are widely employed to evaluate the separation efficiency of charge carriers in photocatalysts [51–53]. The PL spectra of YVO<sub>4</sub>, YVO<sub>4</sub>/Ag, g-C<sub>3</sub>N<sub>4</sub>, YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> and 35 wt%YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag samples are shown in Fig. 8. After 300 nm excitation, all samples exhibit broad emission peaks in the range of 400–550 nm, representing that the photo-excited electrons recombine with holes. As shown in Fig. 8A, the PL intensity decreases after the introduction of Ag NPs. As

for the g-C<sub>3</sub>N<sub>4</sub> sample, the loading of YVO<sub>4</sub> and Ag NPs both make the PL emissions quench (Fig. 8B), which indicates that the charge carries recombination in 35 wt%YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag was largely suppressed compared with g-C<sub>3</sub>N<sub>4</sub> or YVO<sub>4</sub>.

# 3.3. Possible photocatalytic mechanism

On the basis of the above experimental results, the possible mechanism of photocatalytic degradation of MO under visible light irradiation is proposed (Fig. 9). According to the published work, the VB maximum and CB minimum potentials of g-C<sub>3</sub>N<sub>4</sub> were at +1.52 eV and -1.23 eV [25,39], whereas the VB and CB edge potentials of YVO<sub>4</sub> were calculated by the combination of the band gap and UPS measurement to be at -0.81 and +2.61 eV, respectively. For the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> sample, under visible light irradiation, only the electrons in the VB of g-C<sub>3</sub>N<sub>4</sub> can be excited to the CB of g-C<sub>3</sub>N<sub>4</sub> and partially react with  $O_2$  directly to produce  $O_2$  radicals [51–53]. Due to the difference between the CB edge potentials of g-C<sub>3</sub>N<sub>4</sub> and YVO<sub>4</sub>, the excited electrons can be easily transferred from the CB of g-C<sub>3</sub>N<sub>4</sub> to the CB of YVO<sub>4</sub>, greatly suppressing the recombination of photoinduced electrons and holes. For the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag composites, Ag NPs are deposited on the surface of YVO<sub>4</sub> and can act as an electron transportation bridge to facilitate the efficient separation of charge carriers in g-C<sub>3</sub>N<sub>4</sub> [39]. Moreover, the deposition of Ag NPs can significantly enhance the visible-light absorption due to the SPR effect [31,39,54]. As the electrons in the CB of YVO<sub>4</sub> has more negative potential (-0.81 eV) than  $O_2$ /  $\cdot O_2^-$  (-0.33 eV), the electrons were used for the production of  $\cdot O_2^-$ 

radicals by reacting with  $O_2$ . The produced  $\cdot O_2^-$  can accept another electron from  $H^+$  to form  $H_2O_2$ , which can be further activated to  $\cdot$ OH radicals [55,56]. The electrons in the CB of YVO<sub>4</sub> can also directly react with adsorbed  $O_2$  in the presence of  $H^+$  to generate  $H_2O_2$  and then produce  $\cdot$ OH radicals [51–53]. The holes left in the VB of g-C<sub>3</sub>N<sub>4</sub> can directly attack the MO. With increasing the loading amount of YVO<sub>4</sub> over 35 wt%, the excessive YVO<sub>4</sub> could cover the surface of g-C<sub>3</sub>N<sub>4</sub> and limited the light hitting the surface of g-C<sub>3</sub>N<sub>4</sub>. Hence, the optimal loading amount of YVO<sub>4</sub> in the YVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag sample is 35 wt%.

#### 4. Conclusions

In summary, a series of novel YVO $_4$ /g-C $_3$ N $_4$ /Ag composite photocatalyst with different contents of YVO $_4$  were successfully synthesized by a simple hydrothermal and photodeposition approach. The as-prepared composite shows excellent visible light photocatalytic performance and reusability in the degradation of MO due to the SPR effect of Ag NP as well as the charge transfer between the three components. The loading amount of YVO $_4$  was optimized and 35% YVO $_4$ /g-C $_3$ N $_4$ /Ag sample exhibited the highest degradation rate of MO. The possible mechanism of the photocatalytic reaction was also proposed. Based on the results, the YVO $_4$ /g-C $_3$ N $_4$ /Ag composite is expected to be an effective visible-light photocatalyst for environmental remediation.

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